Intrinsic interface mobility characterizing the γ/α–phase transformation in low alloyed steels

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ALEMI (Workshop on alloying element effects on migrating interfaces),
27.-28. March 2008, Musashi Institute of Technology, Tokyo, Japan

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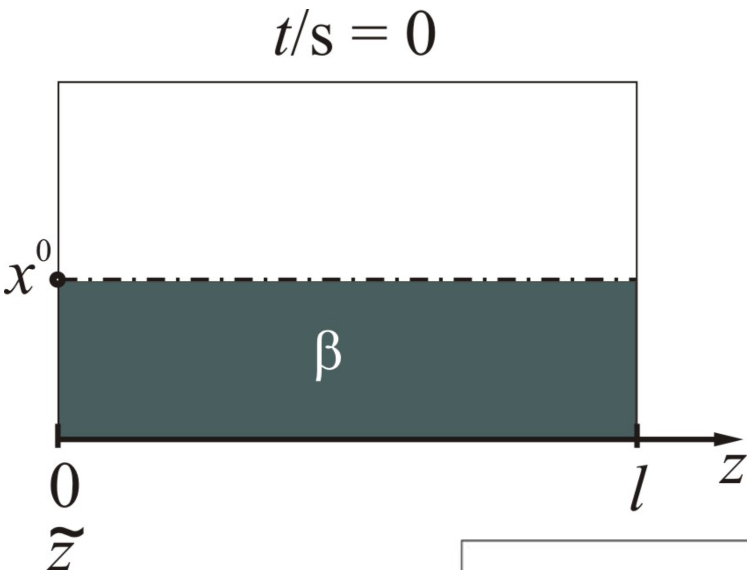
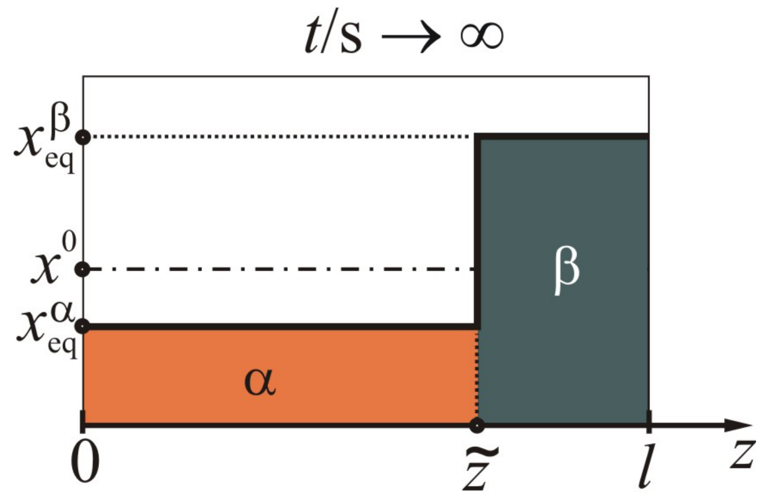
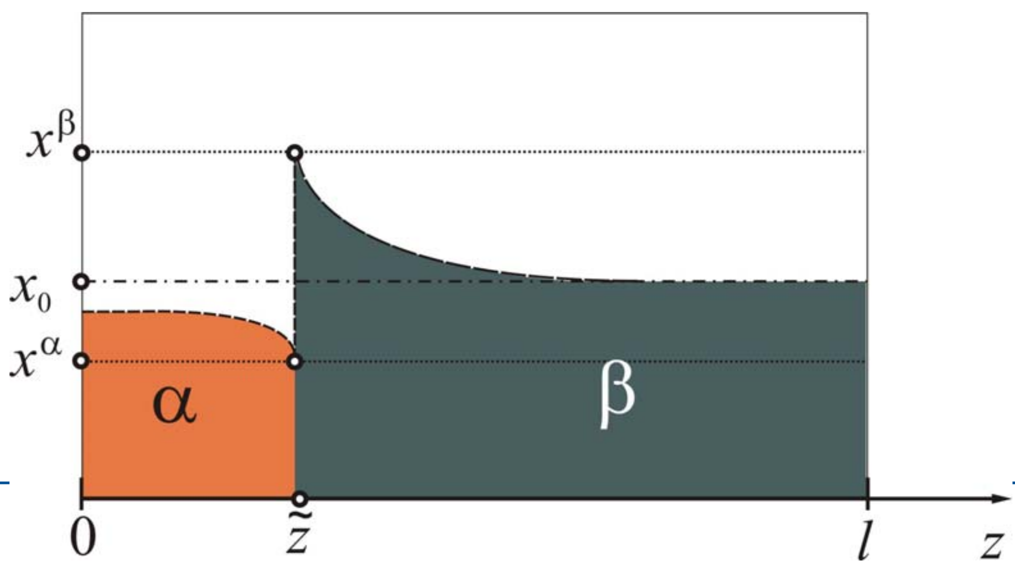
Diffusive phase transformations



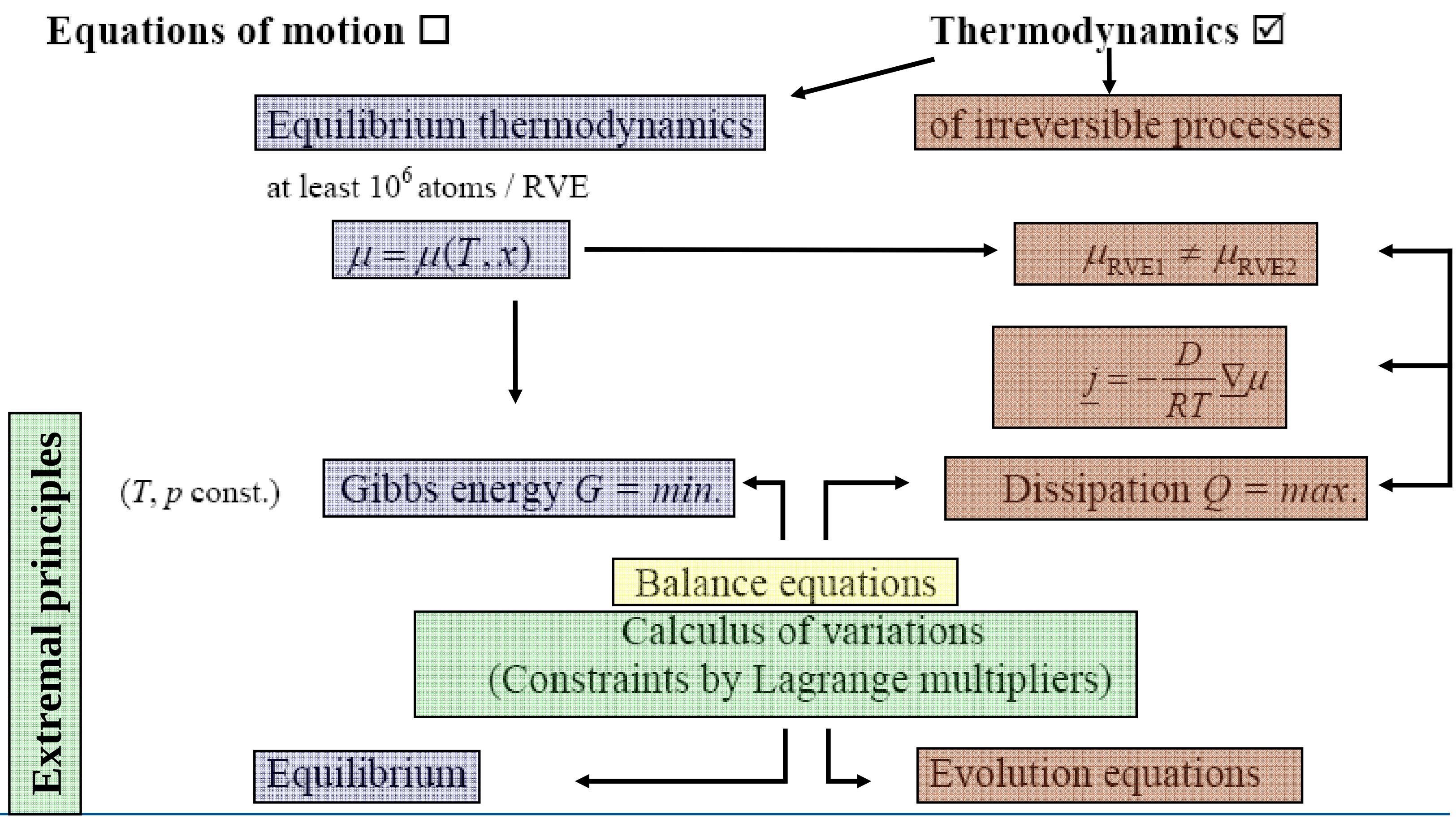




LE
PE
LENP
$M \rightarrow \infty$

Thermodynamic description of multi-particle systems

System: $6 \cdot 10^{23}$ particles



Calculus of variations
(subject to constraints: Lagrange multipliers)

Determine: Extremum of $F(x_1, x_2, \ldots, x_N)$

m constraints $g_j(x_1, x_2, \ldots, x_N) = 0$

$j = 1,2, \ldots , m$; $(m < N)$

By **Lagrange multipliers λ_j:**

Extremum of $F + \sum_{j=1}^{m} \lambda_j g_j$

$$\frac{\partial}{\partial x_i}\left(F + \sum_{j=1}^{m} \lambda_j g_j\right) = 0; \quad i = 1, \ldots , N$$

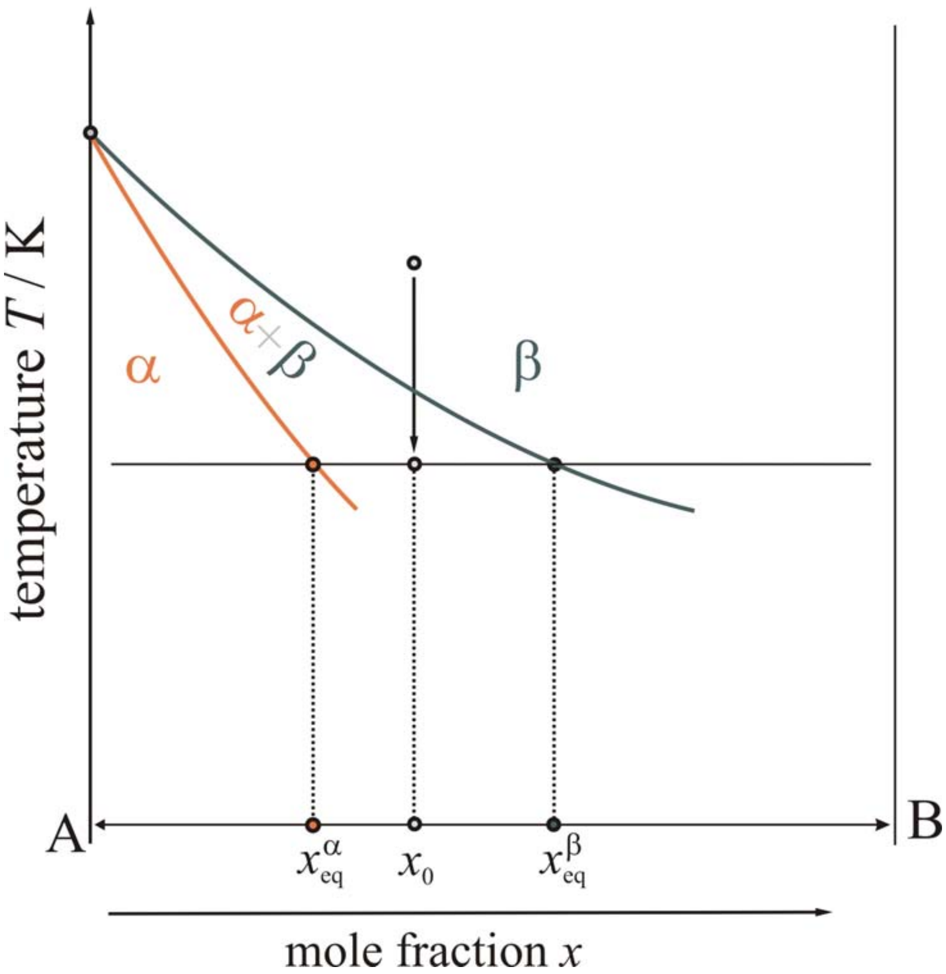
$N + m$ equations

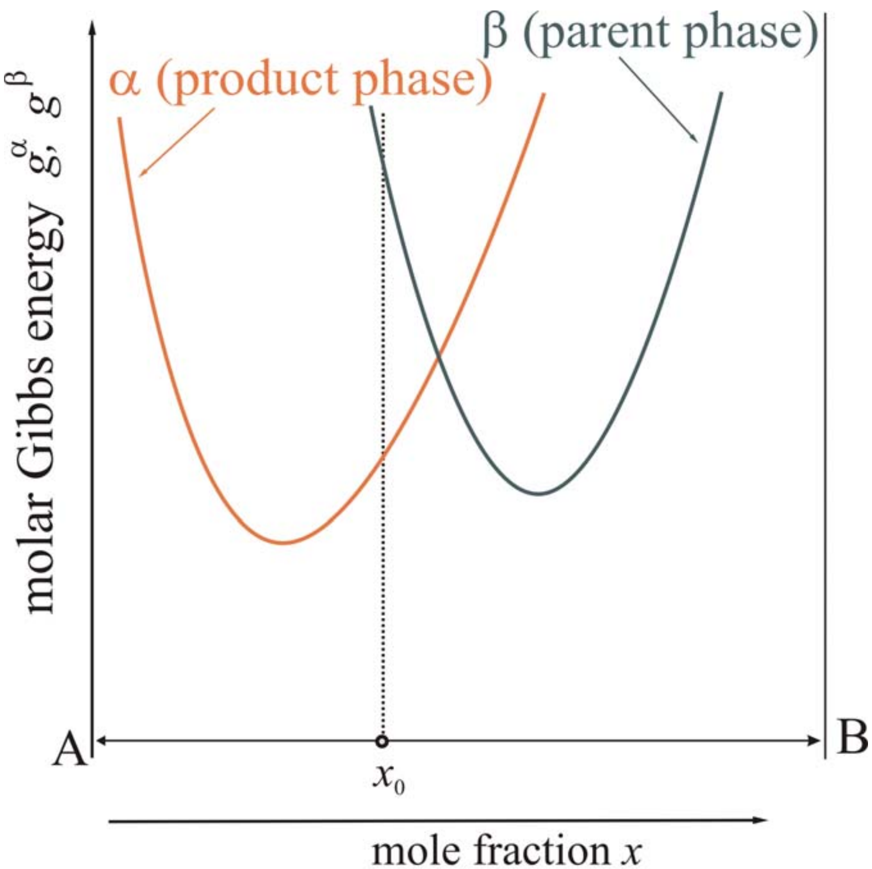
for m unknown λ_j

N unknown x_i

Lagrange: Théorie des Fonctions Analytiques (p. 198, 1797)

Example I:
Phase equilibrium (binary system)





x^{α}_{eq} ? x^{β}_{eq} ? ξ_{eq} ?

Example I:
Phase equilibrium (binary system)

Molar Gibbs energy of the system: $g = g(x^{\alpha}, x^{\beta}, \xi)$

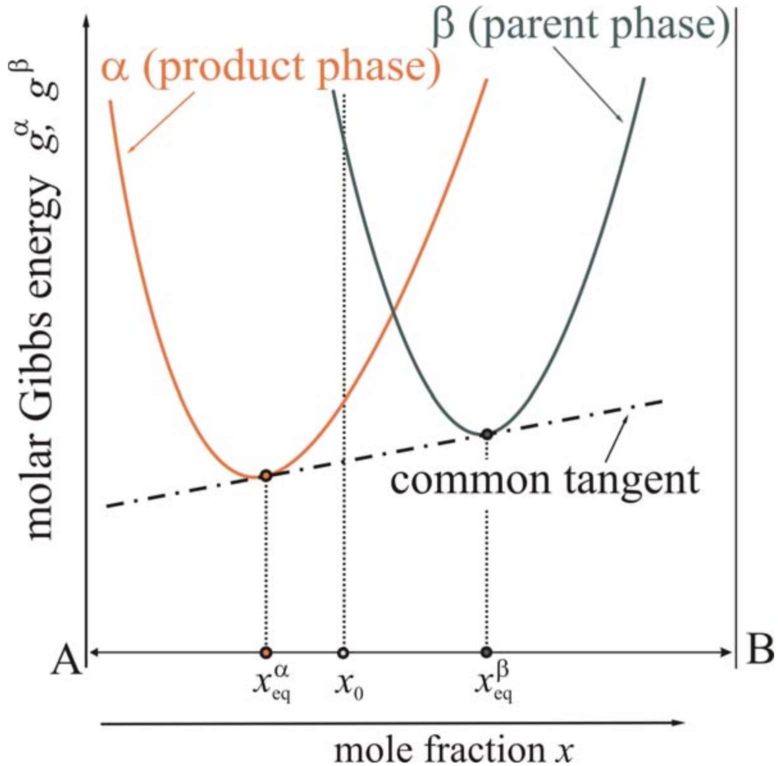
$$g = \xi g^{\alpha} + (1-\xi) g^{\beta}$$ Minimum!

Constraint: $x_0 = \xi x^{\alpha} + (1-\xi) x^{\beta}$

$$\Lambda = \xi g^{\alpha} + (1-\xi) g^{\beta} + \lambda\left(x_0 - \xi x^{\alpha} - (1-\xi) x^{\beta}\right)$$

$$\frac{\partial \Lambda}{\partial x^{\alpha}} = \frac{\partial \Lambda}{\partial x^{\beta}} = \frac{\partial \Lambda}{\partial \xi} = 0$$

$$\lambda = \frac{\partial g^{\alpha}}{\partial x^{\alpha}} = \frac{\partial g^{\beta}}{\partial x^{\beta}} = \frac{g^{\beta} - g^{\alpha}}{x^{\beta} - x^{\alpha}}$$



G. R. Purdy, Y.J.M. Brechet, *Acta Mater.* **44** (1996) 4853-4864

Principle of maximum dissipation Q of the Gibbs energy

Onsager 1931 (Equations for heat conduction)
Onsager 1945 (Equations for diffusion)
Svoboda & Turek 1991 (Evolution equations for characteristic variables q_i)

Closed system, isothermal and isobaric process:
appropriate thermodynamic potential:
Gibbs energy $G(q_1, \ldots, q_N)$

$$\dot{G} = \sum_{i=1}^{N} \frac{\partial G}{\partial q_i} \dot{q}_i$$

Assumption: Dissipation Q of Gibbs energy is a quadratic form of N rates $\dot{q}_i$ of the characteristic variables q_i.

$$Q = \sum_{i=1}^{N} \sum_{k=1}^{N} B_{ik} \dot{q}_i \dot{q}_k$$

B_{ik} considers the kinetic parameter of the material (diffusion coefficients) and the geometry of the system.

Principle of maximum dissipation *Q* of the Gibbs energy

$$\dot{G} = \sum_{i=1}^{N} \frac{\partial G}{\partial q_i} \dot{q}_i$$

$$Q = \sum_{i=1}^{N} \sum_{k=1}^{N} B_{ik} \dot{q}_i \dot{q}_k$$

The extremal principle asserts that the rates $\dot{q}_i$ of the characteristic variables correspond to a maximum of the Gibbs energy dissipation *Q* constrained by the energy balance $Q = -\dot{G}$ and by *m* further constraints.

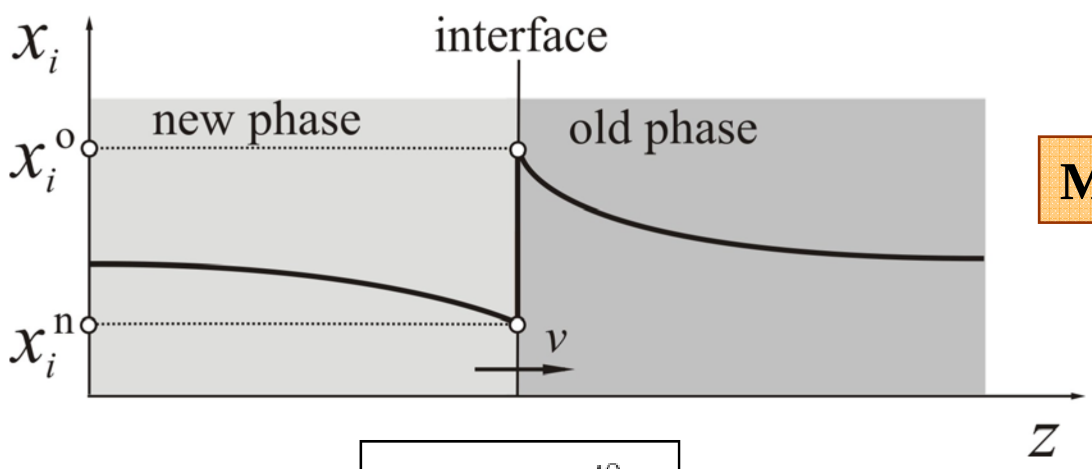
$$\sum_{i=1}^{N} a_{ik}(q_1, ..., q_N) \dot{q}_i = 0$$

$$\frac{\partial}{\partial \dot{q}_i} \left[Q + \lambda \left(Q + \dot{G} \right) + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0$$

$$\frac{\partial}{\partial \dot{q}_i} \left[\dot{G} + \frac{Q}{2} + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0$$

$$\sum_{j=1}^{N} B_{ij} \dot{q}_j + \sum_{k=1}^{m} a_{ik} \beta_k = -\frac{\partial G}{\partial q_i}$$

Example II:
Contact conditions at the sharp interface



$$x_i^{\mathrm{I}} = x_i^{\mathrm{o}} - \frac{j_i^{\mathrm{o}}}{v}\Omega$$

$$[[a]] = a^{\mathrm{o}} - a^{\mathrm{n}}$$

Mass balance at the interface

$$[[(x_i/\Omega)]]v = [[j_i]]$$

Substitutional diffusion

$$\sum_{i=1}^{s} j_i = -j_{\mathrm{va}} \approx 0$$

Assumption: The amount of lattice vacancies is negligibly small, and so is the flux j_{va}.

Example II:
Contact conditions at the sharp interface

$$\dot{G}_{\text{int}} = -\sum_{i=1}^{N} \frac{v}{\Omega} \cdot x_i^{\text{I}}[[\mu_i]]$$

$$x_i^{\text{I}} = x_i^{\text{o}} - \frac{j_i^{\text{o}}}{v}\Omega$$

$$\dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^{\text{o}}[[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^{\text{o}}}{\Omega} v[[\mu_i]]$$

$$Q_{\text{int}} = v^2/M$$

Fluxes of the substitutional components (*i* = 1, … , *s*)

$$\frac{\partial}{\partial j_i^{\text{o}}}\left[\dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2} + \kappa\left(\sum_{k=1}^{s} j_k\right)\right] = 0 \longrightarrow \kappa = -[[\mu_i]] \longrightarrow [[\mu_1]] = [[\mu_2]] = \ldots = [[\mu_s]]$$

E. Gamsjäger, A concise derivation of the contact conditions at a sharp interface, accepted for publication in *Phil. Mag Letters*, 2008.

Example II:
Contact conditions at the sharp interface

$$\dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^{\text{o}}[[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^{\text{o}}}{\Omega} v[[\mu_i]]$$

$$Q_{\text{int}} = v^2/M$$

Fluxes (interstitial components *i*=*s* + 1, …, *N*)

$$\frac{\partial}{\partial j_i^{\text{o}}}\left[\dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2}\right] = 0 \longrightarrow [[\mu_{s+1}]] = [[\mu_{s+2}]] = \; ... \; = [[\mu_N]] = 0$$

Example II:
Contact conditions at the sharp interface

$$\dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^{\text{o}} [[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^{\text{o}}}{\Omega} v [[\mu_i]]$$

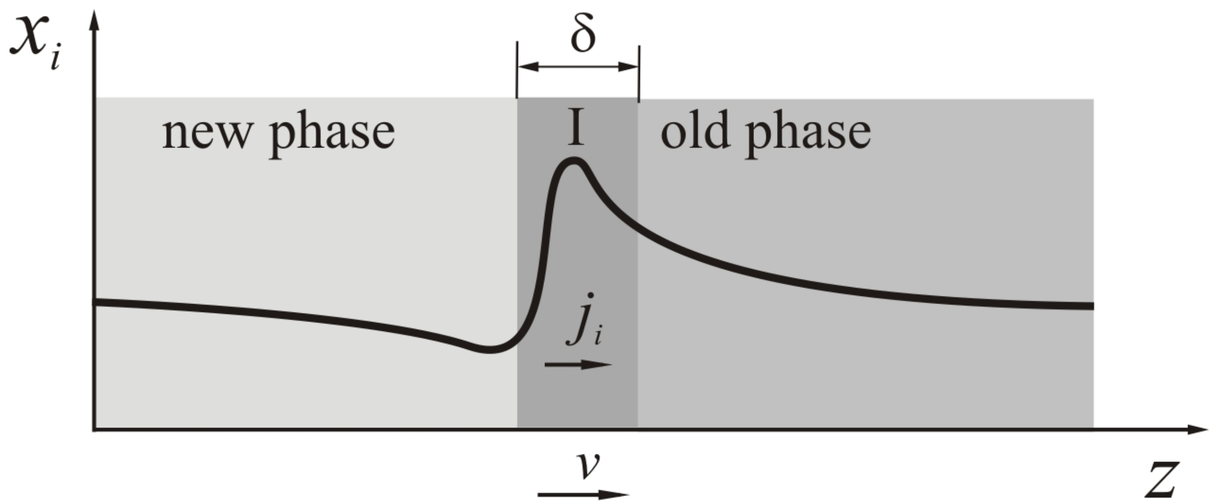
$$Q_{\text{int}} = v^2/M$$

Interface velocity *v*

$$\frac{\partial}{\partial v}\left[\dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2}\right] = 0 \longrightarrow \quad v = \frac{M}{\Omega} \sum_{i=1}^{N} x_i^{\text{o}} [[\mu_i]] = M \Delta f$$

Example III:
Contact conditions at a thick interface

$$G = \frac{1}{\Omega}\sum_{k=1}^{N}\int_0^{\delta} x_k \mu_k \mathrm{d}z$$



$$\dot{G} = \sum_{i=1}^{s}\int_0^{\delta}\left[j_i - (x_i/\Omega)v\right]\frac{\partial \mu_i}{\partial z}\mathrm{d}z$$

$$Q = \sum_{i=1}^{s}\int_0^{\delta}\frac{j_i^2}{A_i}\mathrm{d}z + \frac{v^2}{M}, \quad A_i = \frac{x_i D_i}{\Omega R T}$$

Example III:
Contact conditions at a thick interface

$$\dot{G} = \sum_{i=1}^{s} \int_0^{\delta} [j_i - (x_i/\Omega)v] \frac{\partial \mu_i}{\partial z} \mathrm{d}z$$

$$Q = \sum_{i=1}^{s} \int_0^{\delta} \frac{j_i^2}{A_i} \mathrm{d}z + \frac{v^2}{M}, \quad A_i = \frac{x_i D_i}{\Omega R T}$$

Fluxes of the substitutional components (*i* = 1, … , *s*)

$$\frac{\partial}{\partial j_i} \left[\dot{G} + \frac{Q}{2} + \int_0^{\delta} \kappa \sum_{k=1}^{s} j_k \mathrm{d}z \right] = 0$$

$$\frac{\partial \mu_i}{\partial z} + \frac{j_i}{A_i} + \kappa = 0$$

$$\kappa = -\frac{\sum_{i=1}^{s} A_i \frac{\partial \mu_i}{\partial z}}{\sum_{j=1}^{s} A_j}$$

$$j_i = A_i \left(\kappa - \frac{\partial \mu_i}{\partial z} \right)$$

$$\mu_i(\delta) - \mu_i(0) = -\left(\int_0^{\delta} \kappa \mathrm{d}z + \int_0^{\delta} \frac{j_i}{A_i} \mathrm{d}z \right)$$

Example III:
Contact conditions at a thick interface

$$\dot{G} = \sum_{i=1}^{s} \int_0^\delta [j_i - (x_i/\Omega)v] \frac{\partial \mu_i}{\partial z} \mathrm{d}z$$

$$Q = \sum_{i=1}^{s} \int_0^\delta \frac{j_i^2}{A_i} \mathrm{d}z + \frac{v^2}{M}, \quad A_i = \frac{x_i D_i}{\Omega R T}$$

Interface velocity *v*

$$\frac{\partial}{\partial v}\left[\dot{G} + \frac{Q}{2}\right] = 0 \longrightarrow v = \frac{M}{\Omega} \sum_{i=1}^{s} \int_0^\delta x_i \frac{\partial \mu_i}{\partial z} \mathrm{d}z$$

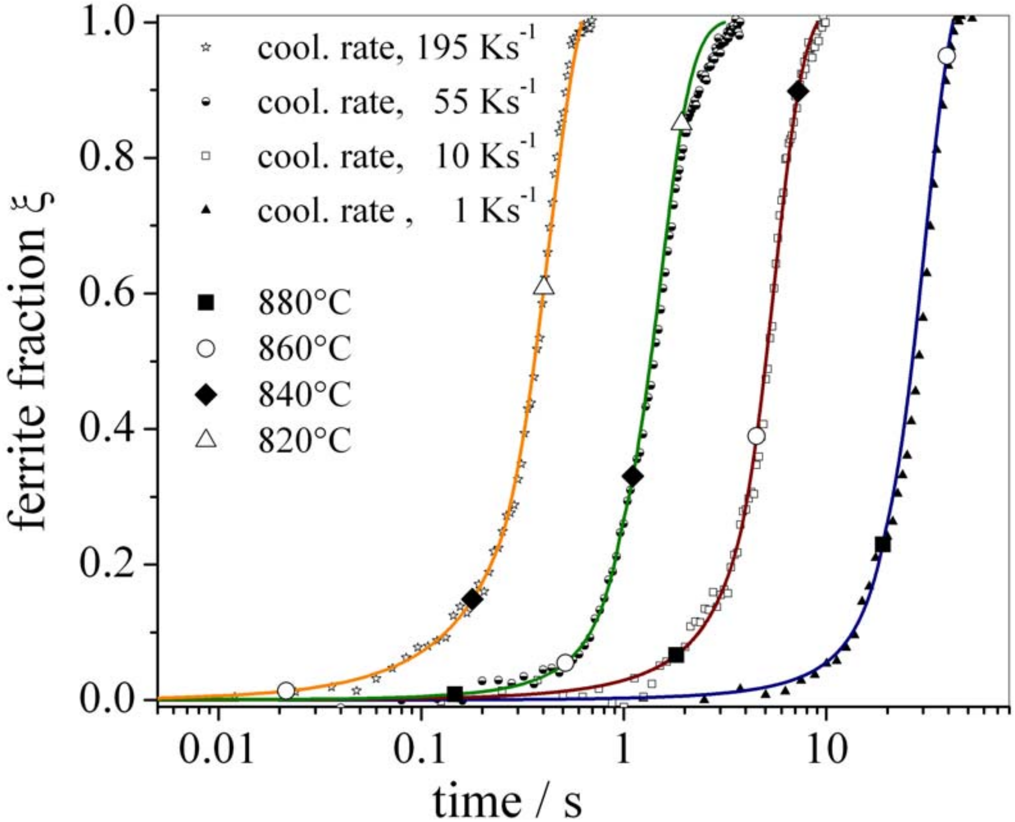
M … intrinsic interface mobility

M_{eff} … effective interface mobility

M. Hillert, *Acta mater*. **52** (2004) 5289–5293.

J. Svoboda, J. Vala, E. Gamsjäger, F.D. Fischer, *Acta mater*. **54** (2006) 3953-3960.

Experiment 1: Ultra-low alloyed C-steel



$$w_C = 20\text{ppm}$$
$$w_{Mn} = 0.11\%$$

$$\xi(t) = \frac{a}{1 + b\exp(-ct)}$$

$$\frac{d\xi}{ds} \cdot \frac{ds}{dt} = \frac{d\xi}{ds}(\text{geometry}) \cdot \frac{ds}{dt}$$

$$v = M_{\text{eff}} \cdot \Delta f$$

M. Militzer, Austenite decomposition kinetics in advanced low carbon steels, Solid Phase Transformations 99, eds. M. Koiwa, K. Otsuka and T. Miyazaki, JIM, Sendai (1999) 1521-1524.

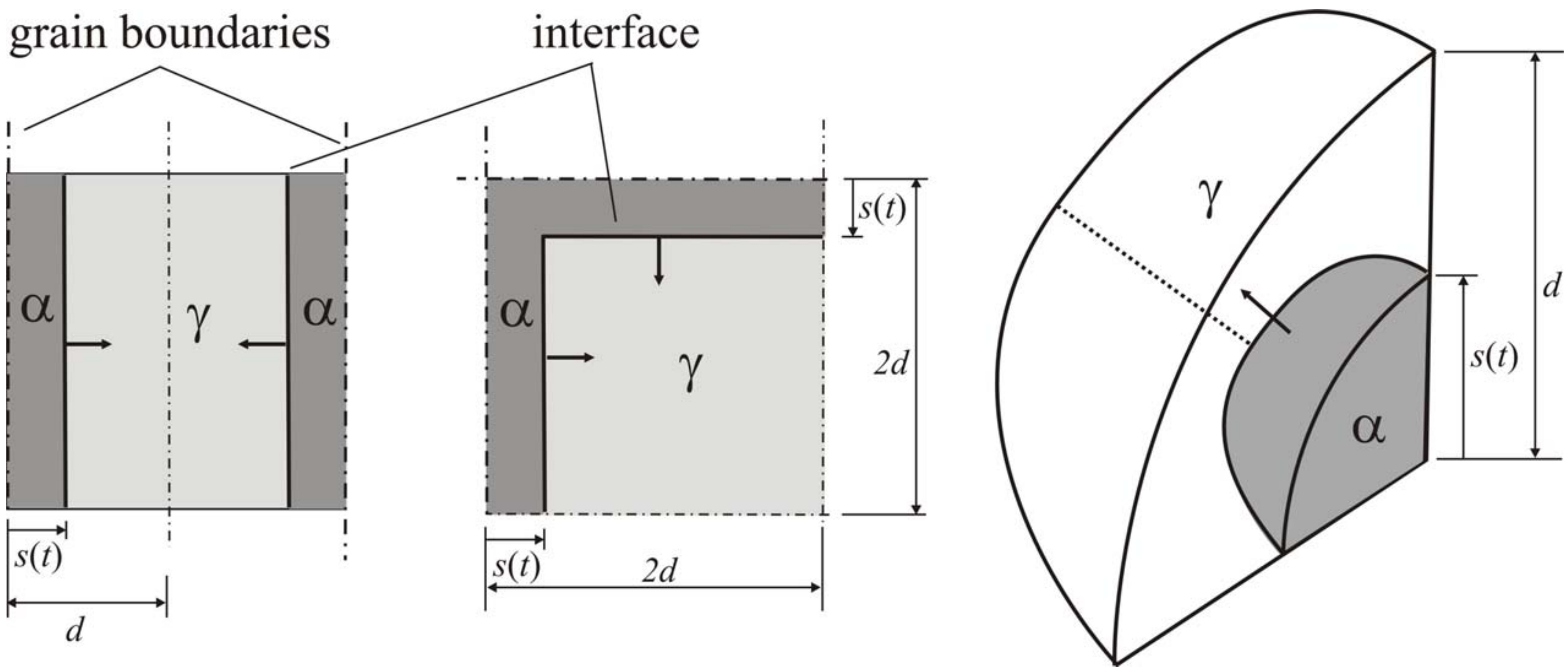
E. Gamsjäger, M. Militzer, F. Fazeli, J. Svoboda, F. D. Fischer: "Interface mobility in case of the austenite-to-ferrite phase transformation", *Comp. Mat. Sci*, **37** (2006) 94-100.

Geometry of the γ/α – phase arrangement

I, Plate

II, 2 Plates

III, Sphere

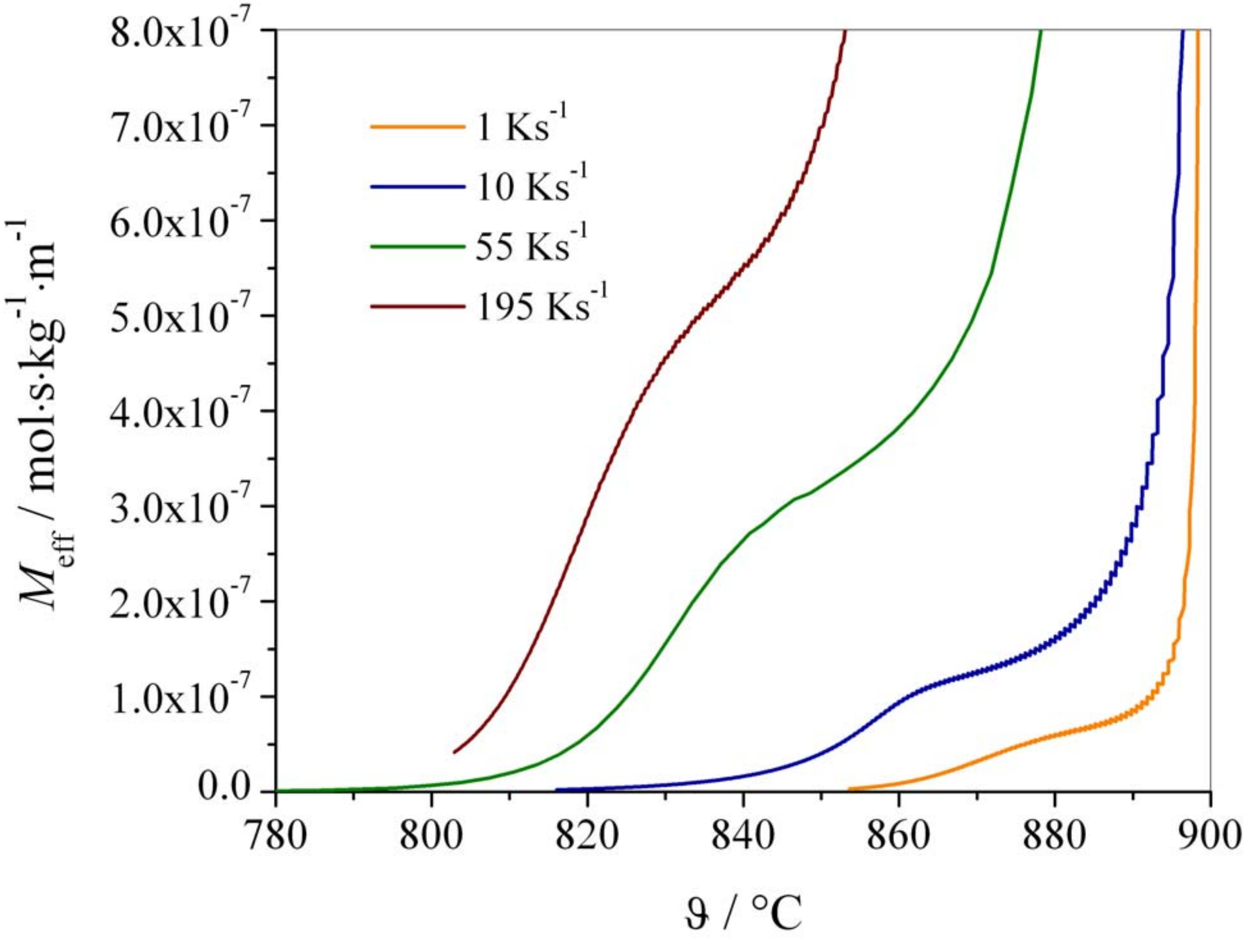


$$M_{\mathrm{eff}} = \frac{d}{\Delta f}\dot{\xi}$$

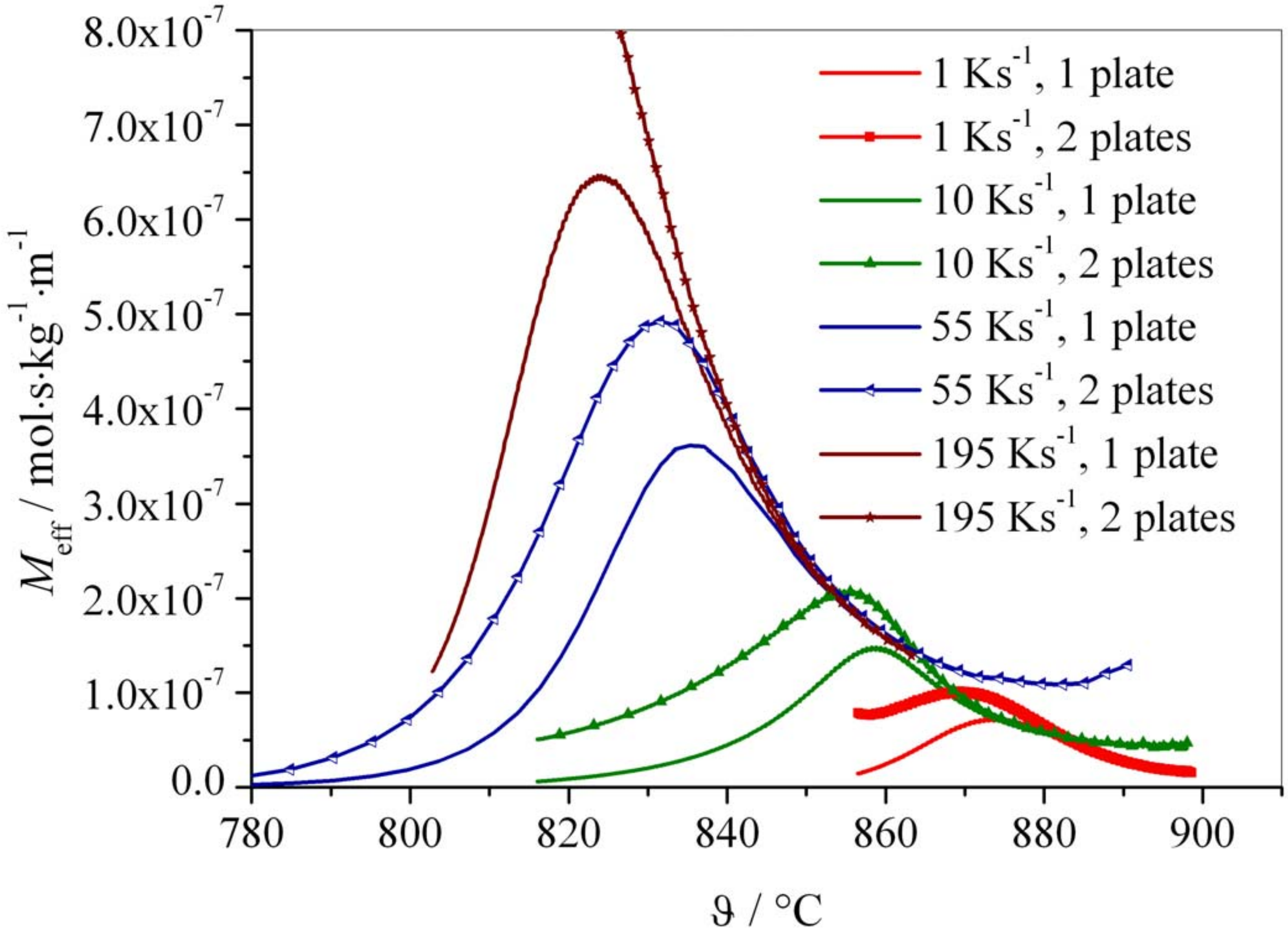
$$M_{\mathrm{eff}} = \frac{2d^2}{(2d - s)\Delta f}\dot{\xi}$$

$$M_{\mathrm{eff}} = \frac{d^3}{3s^2\Delta f}\dot{\xi}$$

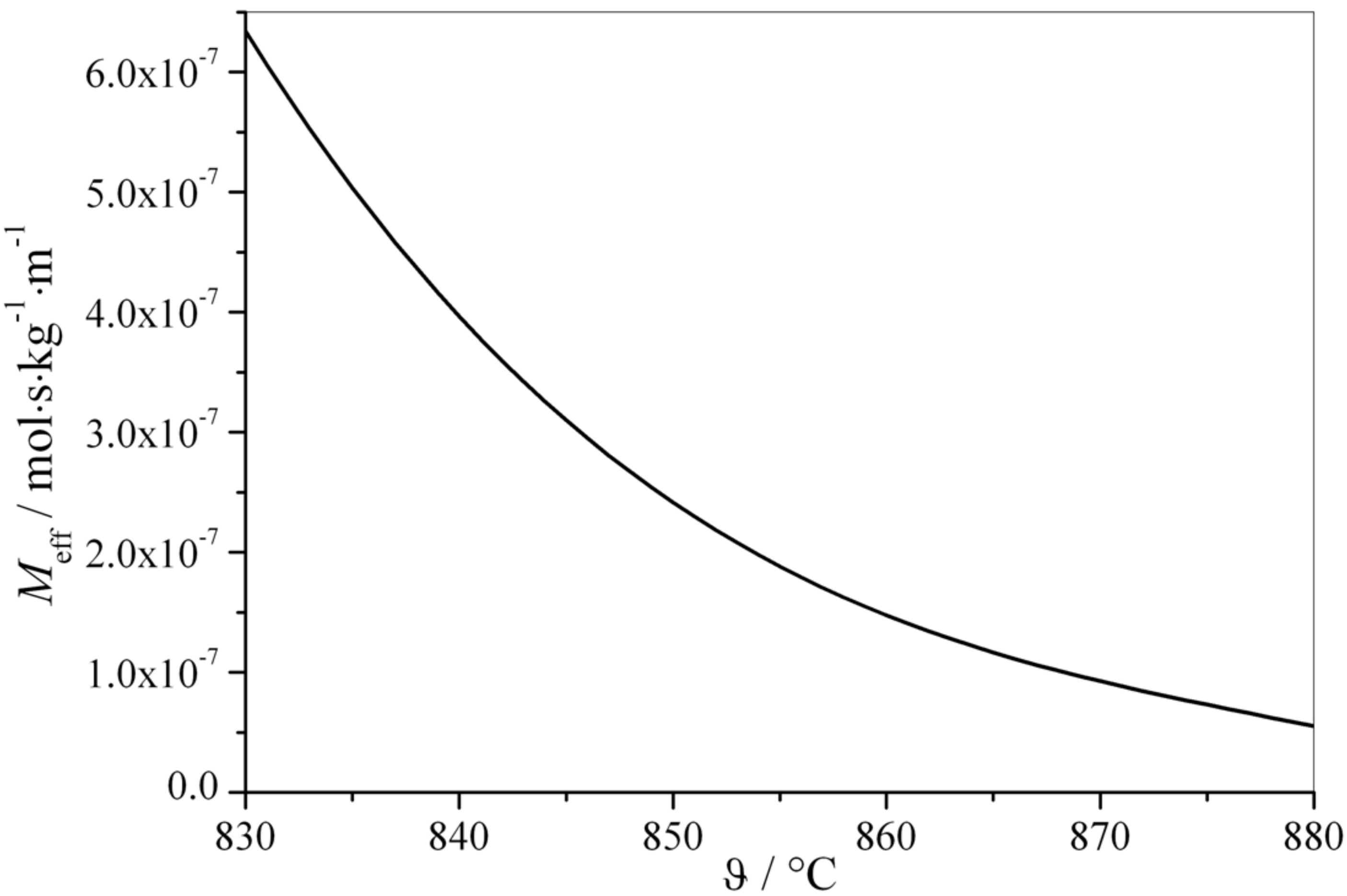
Effective interface mobility for spherical growth



Effective interface mobility for plate-like growth



Master curve



Solute drag

$$v = M_{\text{eff}} \Delta f \longrightarrow v = M\left(\Delta f - \Delta f_{\text{sd}}\right)$$

$$M = M_0 \cdot \exp\left(-\frac{Q_{\text{M}}}{RT}\right) \longrightarrow Q_{\text{M}} \approx 147\,\text{kJ} \cdot \text{mol}^{-1}$$

- $M_0 = 4800\,\text{mol} \cdot \text{s} \cdot \text{kg}^{-1} \cdot \text{m}^{-1}$

  M. Hillert, Diffusion and interface control of reactions in alloys, Metallurgical Transactions 6A (1975) 5-19.

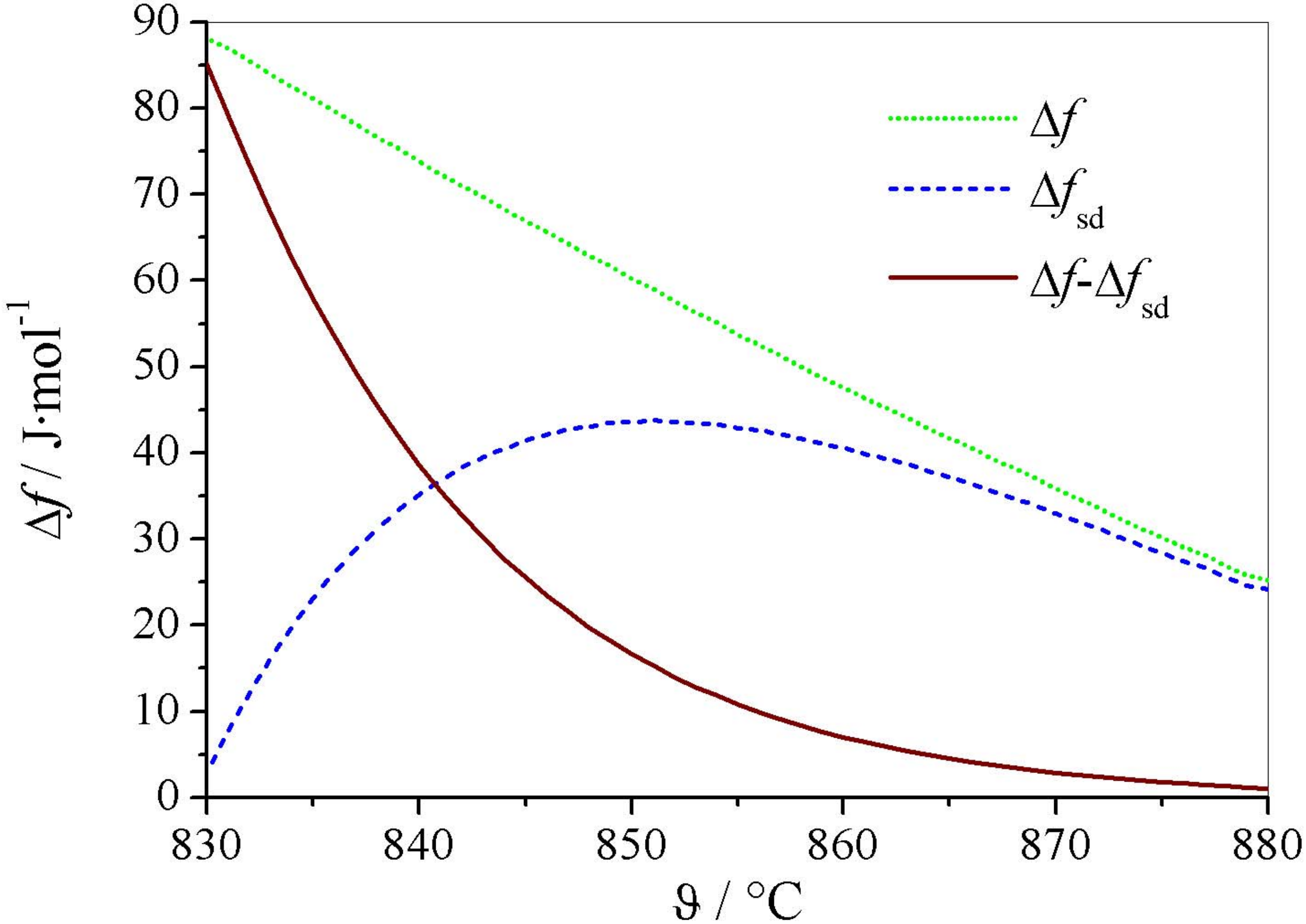
- $M_0 = 0.058\,\text{mol} \cdot \text{s} \cdot \text{kg}^{-1} \cdot \text{m}^{-1}$

  G. P. Krielaart, S. van der Zwaag, Kinetics of γ/α phase transformations in Fe-Mn alloys containing low manganese, Materials Science and Technology 14 (1998) 10-18.

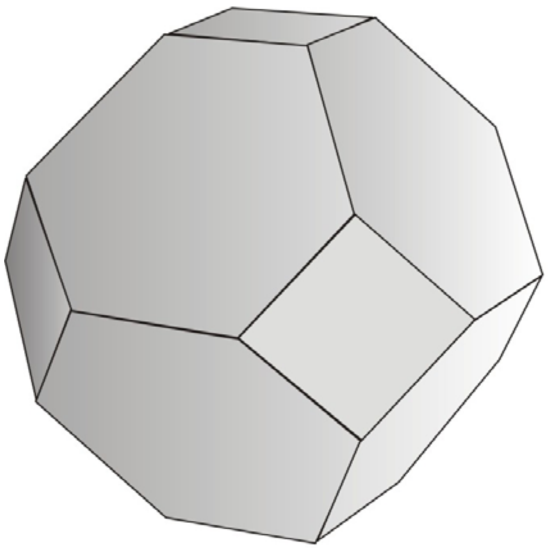
- $M_0 = (6 - 15)\,\text{mol} \cdot \text{s} \cdot \text{kg}^{-1} \cdot \text{m}^{-1}$

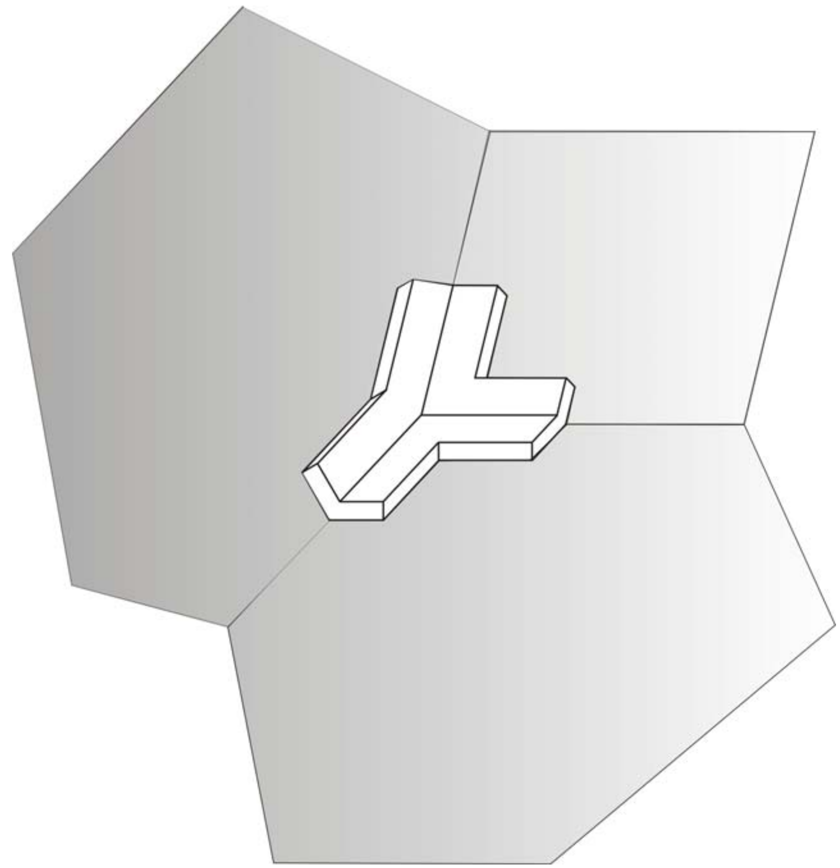
  E. Gamsjäger, M. Militzer, F. Fazeli, J. Svoboda, F. D. Fischer, „Interface mobility in case of the austenite-to-ferrite phase transformation“, Comput. Mater. Sci. 37 (2006) 94-100.

Driving forces



Hierarchical model
(tetrakaidecahedron grains)





Hierarchical model
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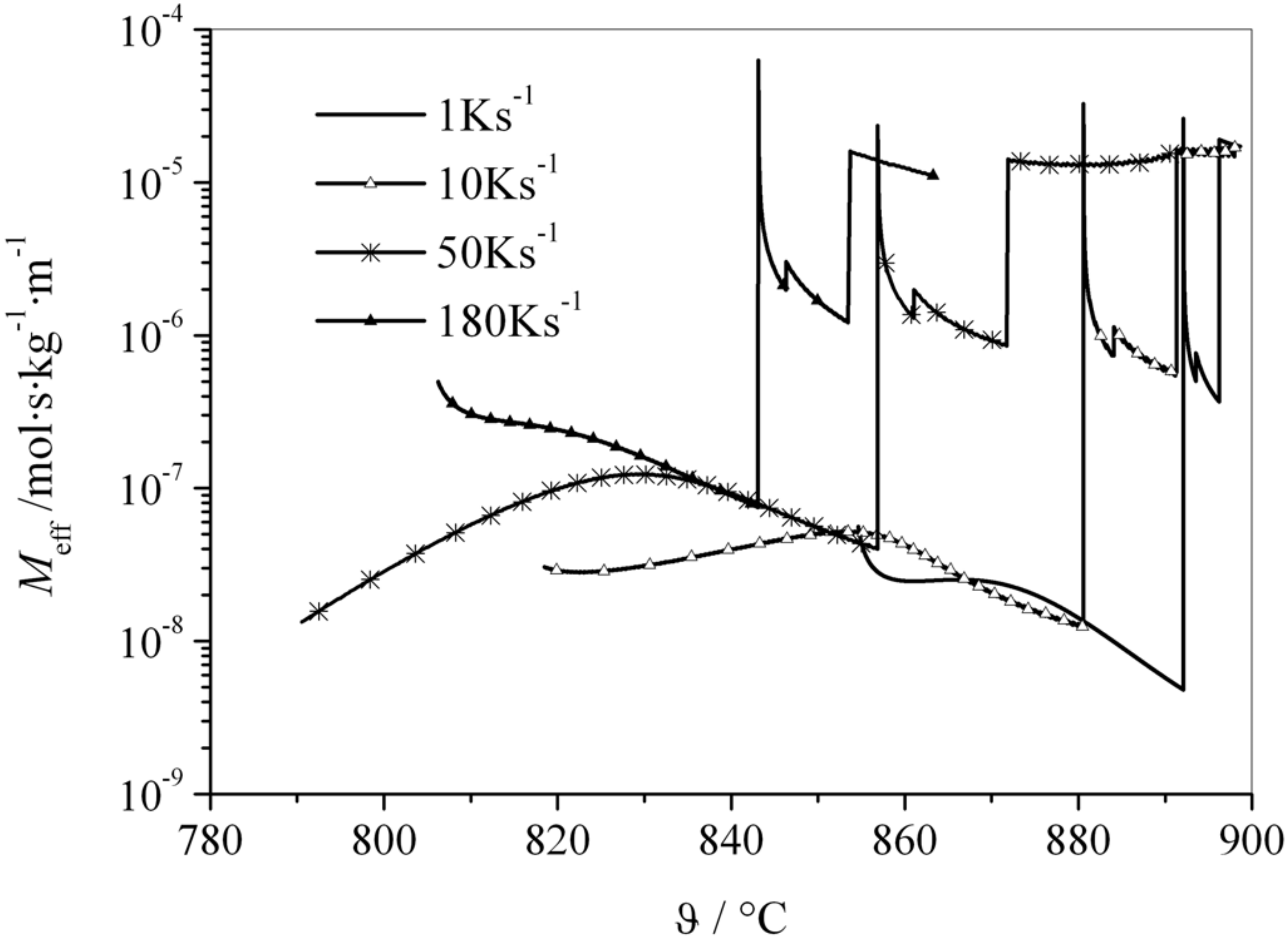
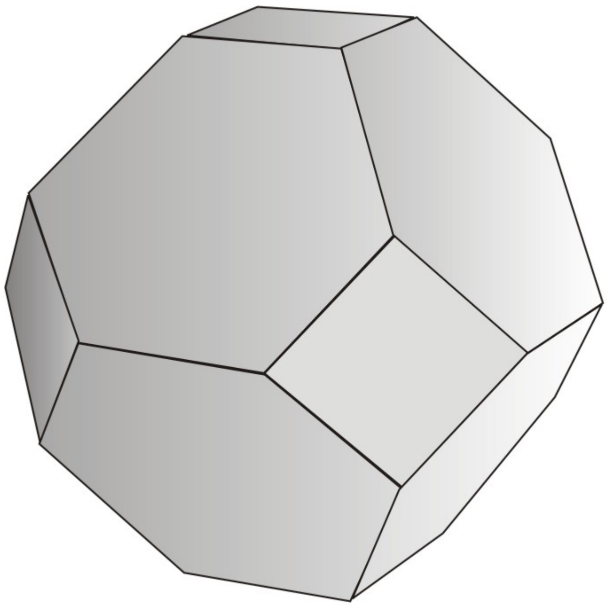
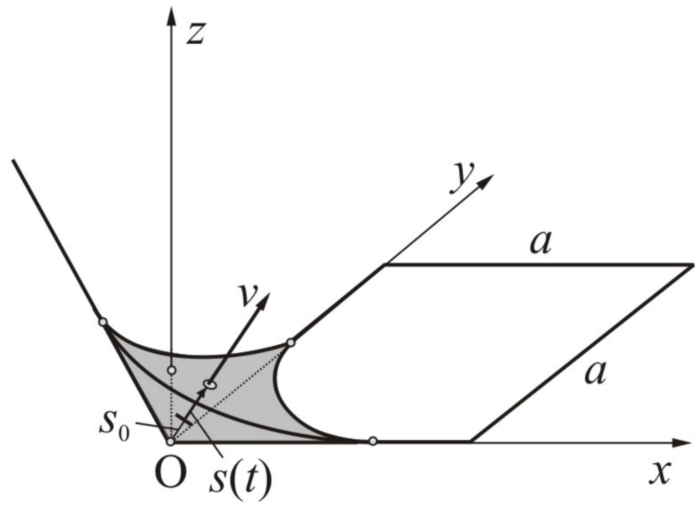
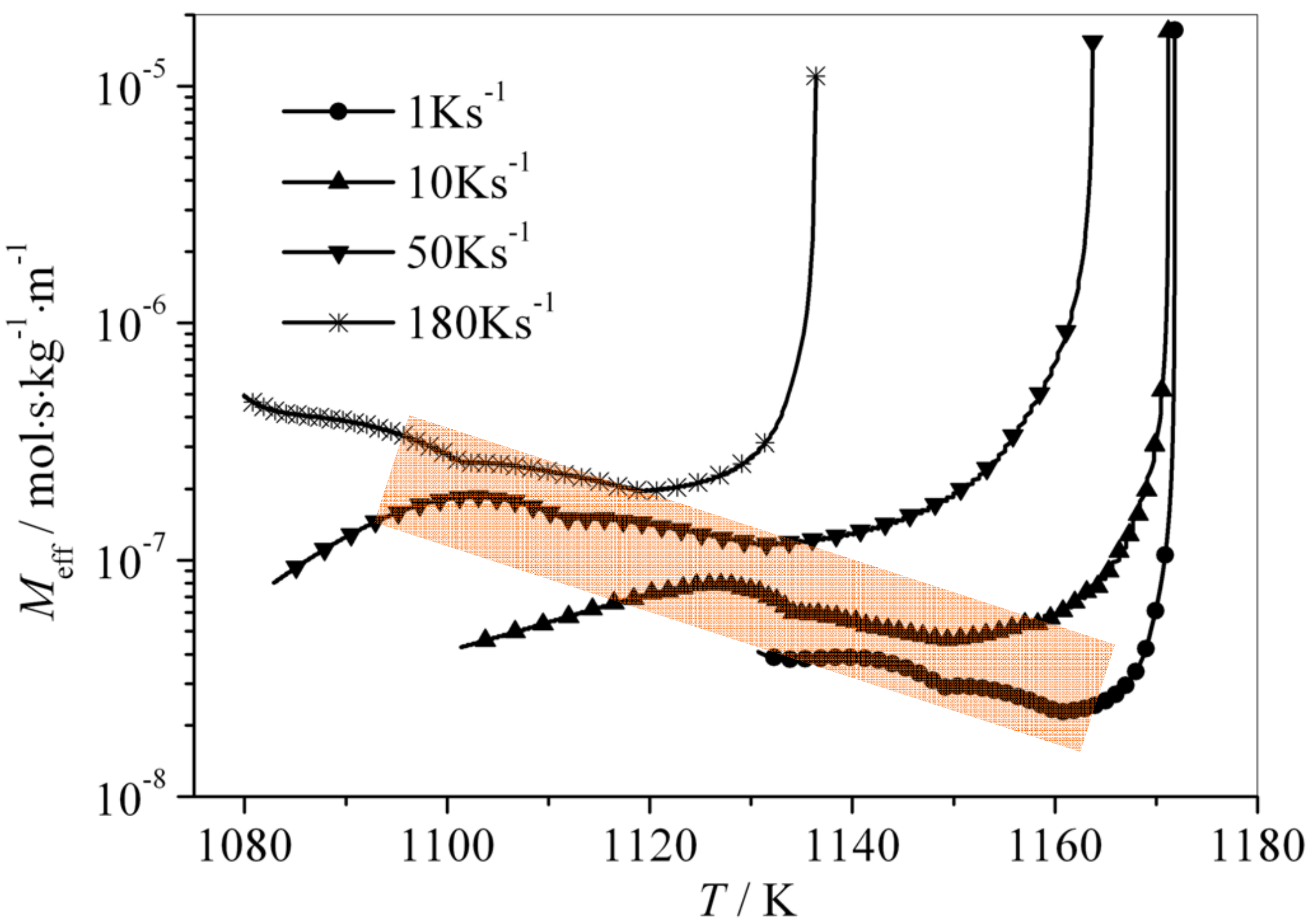


Tetrakaidecahedron model
(Ferrite between tetrakaidecahedron and sphere)

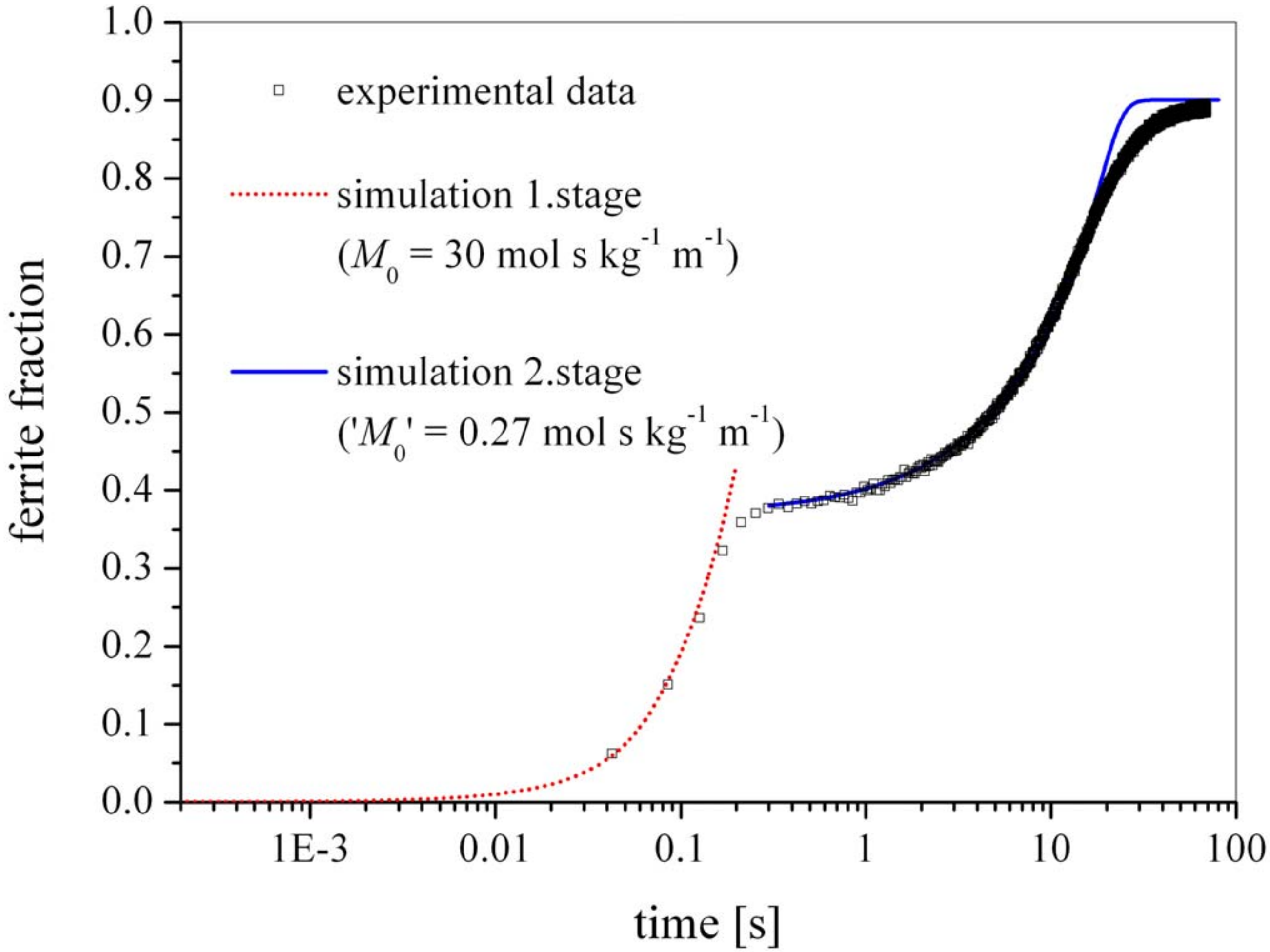




Effective interface mobility as a result of the tetrakaidecahedron model

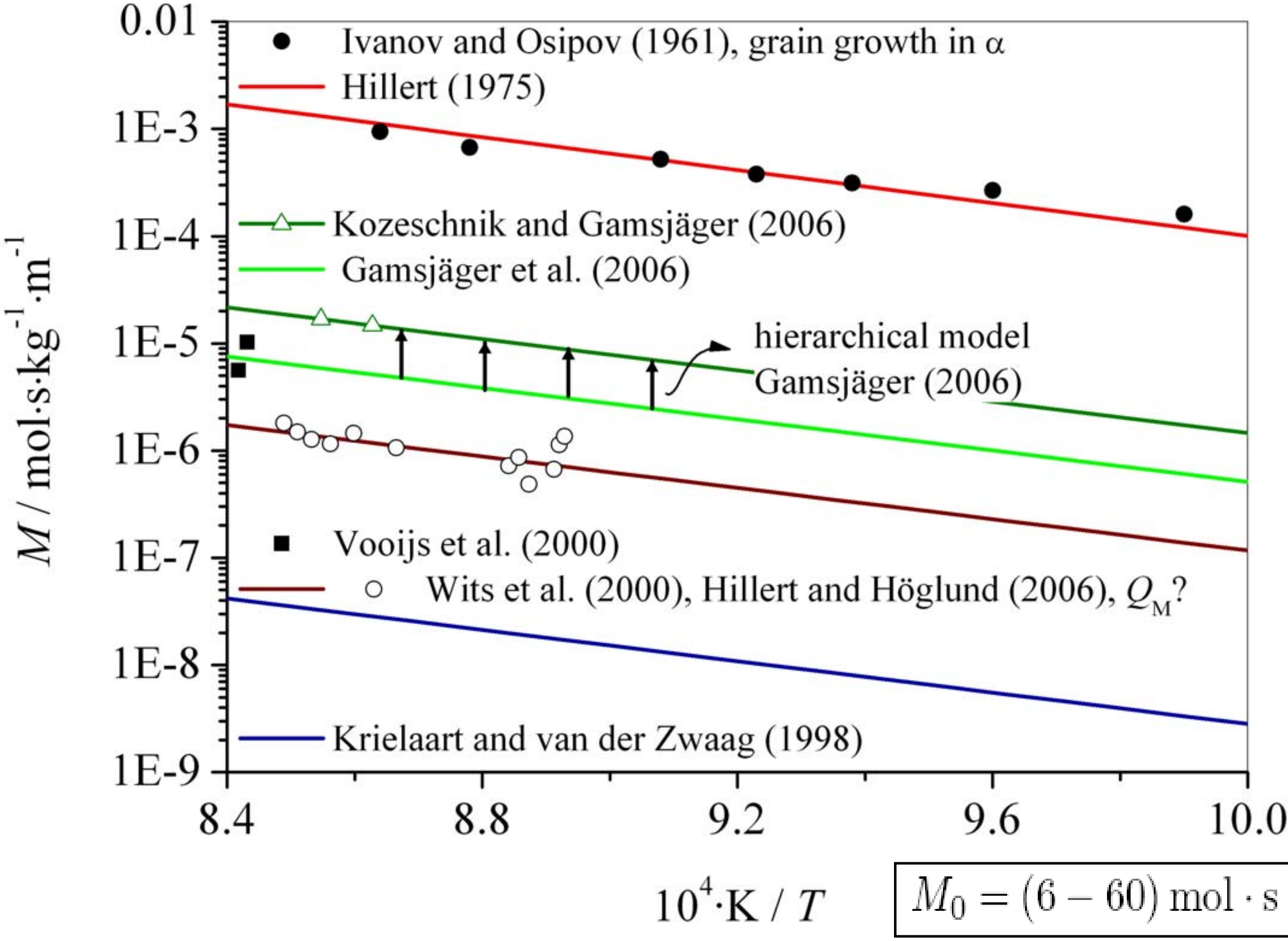


Experiment 2: Fe-C-alloy
1. stage and 2. stage



E. Kozeschnik, E. Gamsjäger, *Metall. Mater. Trans.* **37A** (2006) 1791-1797.

Intrinsic interface mobility *M*
A literature survey



$$M_0 = (6 - 60)\ \mathrm{mol \cdot s \cdot kg^{-1} \cdot m^{-1}}$$

Conclusions and Outlook

➔ **Sharp & thick interface models in the view of non-equilibrium thermodynamics**

<u>Results: sharp interface</u>

❖ **Substitutional components**

$$[[\mu_1]] = [[\mu_2]] = \ ... \ = [[\mu_s]]$$

❖ **Interstitial components**

$$[[\mu_{s+1}]] = [[\mu_{s+2}]] = \ ... \ = [[\mu_N]] = 0$$

❖ **Interface velocity**

$$v = \frac{M}{\Omega} \sum_{i=1}^{N} x_i^{\circ} [[\mu_i]] = M \Delta f.$$

➔ **Estimation of the intrinsic mobility**

❖ Evaluation of experimental data by transformation models.

<u>Next tasks:</u>

➔ Application of the principle of maximum dissipation to further problems in materials science.